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SULPHATE RESISTANCE OF BLENDED (SLAG) CEMENT

Engineering
Materials
Office

SULPHATE RESISTANCE OF BLENDED (SLAG) CEMENT

by

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SUMMARY

Two series of tests were carried out to determine sulphate resistance of 1:0, 3:1 and 1:1 blends of Type 10 Portland cement and cementitious hydraulic slag. One of the test series was in accordance with the standard sulphate resistance test procedure (CSA Standard CAN 3-A5-M77). The other involved storage of mortar prisms, containing no sulphate added to the mix, in a sulphate solution (SO_3 = 24,800 ppm). The Type 10 cements used in the tests had a C_3A content of 4.69 to 11.62 percent. A type 50 cement was included for comparison purposes.

The tests showed that each blend had a higher sulphate resistance than Type 10 cement used in the blend and that the resistance increased with an increase in the slag content. The resistance of the 1:1 blend was approximately the same as that of Type 50 (sulphate resisting) cement.

The report recommends the use of Type 10 cement-slag blends where sulphate resistance is required.

SULPHATE RESISTANCE OF BLENDED (SLAG) CEMENT

INTRODUCTION

The Standard Slag Cement Co., Fruitland, Ontario, has been producing cementitious hydraulic slag complying with CSA Preliminary Standard A 363-M 1977 requirements for several years. The slag has been approved by this Ministry for use in precast catchbasins (MTC Form 1351) and pipes (MTC Form 1820) up to 65 percent of the total cementitious material. Approval for use of the material in general concrete construction is now being considered and a decision is expected this summer.

The effect of this slag on the sulphate resistance of concrete was studied for the manufacturer by McMaster University, Hamilton. The study was carried out under the direction of Dr. J.J. Emery and was reported by Mr. C.A. Low in his thesis for the degree of Master of Engineering "Sulphate Resistance of Slag Cements", February, 1980 [1]. The main conclusion of the study was that sulphate resistance of a blend of 50 percent slag and 50 percent Type 10 cement was equal to that of Type 50 (sulphate resisting) cement. Because of this conclusion, the Standard Slag Cement Co. has requested the Ontario Ministry of Environment and this Ministry to approve the use of the blend where Type 50 cement is specified. This request resulted in a decision to carry out a series of sulphate resistance tests to confirm the McMaster University's findings. The tests were carried out during 1980/81 and the outcome is reported herein.

OBJECTIVES

The objective of the investigation was to determine sulphate resistance of 1:0, 3:1 and 1:1 blends of Type 10 Portland cement and the slag by mass. The slag was to be tested with Type 10 cements with low to very high C_3A content. Type 50 cement was included for comparison purposes.

TEST METHODS FOR DETERMINING SULPHATE RESISTANCE

The standard test method for the evaluation of sulphate resistance of Portland cements [2, 3] involves the addition of gypsum to the mortar at the time of mixing so that the total amount of SO_3 is 7 percent by mass of the cement-gypsum blend, and storage of the prisms in distilled water. The prisms are one day old at the time they are placed in the water. The amount of the expansion of the prisms in the water determines the resistance to sulphate attack. The validity of this method for use for blended cements is questioned because the hydration

of the slag in a blend takes some time to achieve equal impermeability to otherwise comparable Portland cement mortars [4]. Therefore, other test methods [1, 4, 5] have been used for blended cements. The methods involve the immersion of test specimens, containing no added SO_3, in sulphate solution.

This investigation involved the following two methods in the evaluation of the sulphate resistance of the slag-Type 10 cement combinations:

i) The standard method [2] employing 25 mm x 25 mm x 160 mm prisms

and ii) The sulphate solution method. Six prisms were made as for the standard method except that no gypsum was added to the mix. They were cured in the moulds in the moisture cabinet for the first 48±1h and then, after demoulding, they were placed in a lime saturated water at 23±1.5°C for 26d. In addition to the prisms, three 50 mm cubes were made from each mix and tested for compressive strength at 28d. The strength of each mix was within 27.6 - 32.8 MPa. Three of the six prisms were immersed at 28d in a solution containing 99.8 g of $Na_2SO_4 \cdot H_2O$ in 1000 mL of distilled water (SO_3 - 24800 ppm) and the other three in distilled water. The volume of the prisms to the volume of the solution was 1:4. The water and the solution were replaced each week; the containers were covered to avoid evaporation. The specimens were measured for length before immersion in the solution and then at intervals.

CEMENTS

The chemical and physical properties of the test slag and the cements used in this investigation are shown in Table A. The cements were from four plants and varied in C_3A content from 1.48 (Type 50) to 11.65 percent.

TEST RESULTS

Generally, each test result is the average of six (standard test) or three (prisms stored in SO_3 solution) individual test results. Where any of the individual test results differed by more than 20 percent from the average, it was rejected.

Standard Test - The results of this test are presented in Table B and Figure 1 for cements A, B and D[1], and in Table C and Figure 2 for cements C and D. It is evident from Figure 1 and 2 that the expansion of the prisms without the slag, as expected, increased with an increase in the C_3A content of the cements. The prisms with the slag expanded substantially less

than the prisms without the slag and the same cement. In all cases, the prisms with the 1:1 ratio of Type 10 cement to slag expanded less than those with the 3:1 ratio. It is clear from Figure 1 and 2 that the amount of the expansion of the prisms with the slag depended not only on the cement to slag ratio but also on the C_3A content in the cement. None of the prisms with the slag expanded less than the Type 50 cement prisms (D'). The Type 50 cement contained only 1.48 percent of C_3A while the cement-slag combinations contained at least 2.35 percent of C_3A (cement D, 1:1 cement to slag ratio).

Sulphate Solution - The test results are shown in Table D and Figure 3. As in the standard test, the performance of the prisms depended on the C_3A content. The prisms expanded at a much slower rate than those in the standard test and a much longer exposure period was necessary to obtain clear differences between the cements. However, since the prisms at the time of placing them in the sulphate solution were matured (28d) to a large degree, and thus the sulphate attacked matured paste, this test better simulates field conditions than the standard test. All the prisms with 1:1 and 3:1 cement to slag ratio have expanded slightly less than the ones with the Type 50 cement. The expansion of these prisms at 252d was maximum 0.039 percent while the expansion of those with Type 50 cement was 0.042 percent.

The expansion of each set of the companion prisms stored in water varied considerably during the exposure. It was regressive at some ages. However, the highest expansion of each set was at the end of the exposure (253 d) and was within 0.016-0.027 percent. This variation was considered normal for the test at this level of expansion.

This sulphate solution test was similar to the one employed by McMaster University (1). The test results confirm McMaster University's findings that a 1:1 blend of Type 10 cement to the slag has approximately the same sulphate resistance as Type 50 cement.

CONCLUSIONS

This laboratory investigation showed that:

i) blends of Type 10 cement and cementitious hydraulic slag manufactured by Standard Slag Cement Co. had a substantially higher sulphate resistance than Type 10 cement used in the blend. This superiority of the blends was determined by the standard test (CSA CAN3-A5-M77) and the test involving storage of the specimens in a sulphate solution

ii) the sulphate resistance of the blends increased with an increase in the slag content.

iii) the blends with Type 10 cement containing high amounts of C_3A benefited more from the addition of the slag than the blends with Type 10 cement containing small amounts of C_3A.

iv) all the blends had a sulphate resistance, as measured by the test involving storage of the specimens in the 24800 ppm sulphate solution, approximately equal to that of Type 50 (sulphate resisting) cement. This confirms the findings by McMaster University (1).

RECOMMENDATIONS

It is recommended that the use of Type 10 cement and cementitious hydraulic slag blends be allowed where sulphate resistance is required. The ratio of slag to Type 10 cement should depend on the severity of sulphate exposure. A blend of Type 10 cement with a C_3A content of up to approximately 12 percent and cementitious hydraulic slag from Standard Slag Cement Co. in a ratio of 1:1 by mass has approximately the same sulphate resistance as Type 50 cement.

The recommendation is for the slag from Standard Slag Cement Co. Slag from any other source should be tested before it is used in blends to be exposed to sulphate attack.

REFERENCES

1. C.A. Low, "Sulphate Resistance of Slag Cements", A Thesis Submitted to the School of Graduate Studies in Partial Fulfillment of the Requirements for the Degree Master of Engineering, McMaster University, Hamilton, February, 1980.

2. CSA Standard CAN3-A5-M77, Portland Cements.

3. ANSI/ASTM C 452-75, Standard Test Method for Potential Expansion of Portland Cement Mortars Exposed to Sulphate.

4. ASTM Committee C01.29, Test Method for Resistance of Mortar Bars Made Using Hydraulic Cement to Combined Sodium and Magnesium Solution, Draft No. 6, Dec. 26, 78.

5. Frodingham Cement Co. Ltd., Rapid Tests for Sulphate Resistance in West Germany, English Translation, Sept. 17, 1979.

TABLE A Physical and Chemical Properties of Cements

Property		Type 10 Cement					Type 50 Cement	Cementitious Slag	Test Method
		Plant A 79-L-16 Batch 182	Plant A' 80-L-10 Batch 196	Plant B 79-L-14 Batch 179	Plant C 79-L-20 Batch 185	Plant D 79-L-18 Batch 183	Plant D' 80-L-01 Batch 187	Plant E 79-L-19 Batch 184	
Physical Properties									
Fineness, pass 75 μm sieve, %		95.8	94.2	96.4	96.4	96.6	98.0	90.2	CSA CAN3-A5-M77
Fineness, Blaine, m^2/kg		352.6	340.4	366.8	362.3	344.2	373.5	422.8	ASTM C204-79
Setting, time, min		110	100	115	80	95	135	-	CSA CAN3-A5-M77
Soundness, exp., %		0.104	0.034	0.104	0.022	0.066	0.180	-	
False set, penetr., mm at 11 min/after remixing		50/50	35/50	42/50	50/50	50/50	50/50	50/50	ASTM C359-75
Compressive Strength, MPa	3d	23.8	22.3	16.4	23.8	23.1	16.5	4.3	CSA CAN3-A5-M77
	7d	29.7	27.8	21.3	29.2	27.4	23.6	9.9	
	28d	35.0	36.8	27.8	35.9	34.5	33.8	15.8	
Chemical Properties									
Loss on ignition, %		2.18	1.99	1.10	1.17	0.69	0.87	0.98	
Insoluble residue, %		0.43	0.52	0.10	0.30	0.11	0.07	-	
C_3A, %		11.62	10.07	11.08	6.96	4.69	1.48	-	
SO_3, %		3.86	3.97	3.35	3.31	2.80	1.90	0.12	
MgO, %		2.94	2.70	2.22	2.47	3.40	3.23	12.10	CSA CAN3-A5-M77
Al_2O_3, %		5.87	5.42	5.90	4.54	3.61	3.09	7.04	
Fe_2O_3, %		2.33	2.54	2.70	3.00	2.89	3.97	1.40	
CaO, %		62.08	61.68	62.74	63.29	64.10	63.62	37.92	ASTM C114-77
SiO_2, %		19.55	20.80	20.84	21.16	21.52	22.56	38.94	
Na_2O, %		0.24	0.25	0.20	0.33	0.47	0.43	0.25	
K_2O, %		0.94	0.65	0.95	0.73	0.47	0.35	0.33	
Alkali content, %		0.86	0.68	0.83	0.81	0.78	0.66	0.47	
Oxides ratio		$\frac{CaO + MgO + Al_2O_3}{SiO_2}$						1.465	CSA A363-M1977

TABLE B Sulphate Resistance
Test Results, Cements A,B,D',
CSA CAN3-A5-M77 Test

Age d	Cement A		Cement B			Cement D'
	Cement to Slag Ratio by Mass					
	1:0	1:1	1:0	3:1	1:1	1:0
	Expansion, %					
14	.074 .076 .076 .076 .066 .076 0.074	.058 .066 .054 .052 .050 .052 0.055	.054 .050 .054 .052 .048 .048 0.051	.046 .050 .054 .054 .054 .054 0.052	.046 .048 .046 .042 .050 .048 0.047	.012 .016 .012 .012 .014 .018 0.013
28	.116 .120 .120 .116 .116 .116 0.117	.070 .064 .068 .062 .060 .064 0.065	.094 .090 .092 .092 .088 .092 0.091	.074 .076 .080 .082 .084 .076 0.079	.066 .068 .064 .062 .070 .064 0.066	.014 .018 .012 .010 .014 .018 0.013
42	.162 .166 .164 .162 .162 .162 0.163	.080 .076 .078 .072 .074 .074 0.076	.126 .116 .122 .124 .118 .122 0.121	.090 .090 .096 .096 .098 .092 0.094	.074 .074 .070 .070 .066 .070 0.071	.018 .020 .016 .012 .018 .022 0.019
56	.210 .216 .220 .210 .216 .208 0.213	.080 .084 .086 .078 .080 .080 0.081	.166 .158 .166 .168 .164 .166 0.165	.112 .112 .116 .118 .120 .114 0.115	.084 .074 .082 .080 .084 .080 0.081	.022 .024 .022 .018 .022 .024 0.022
84	.330 .352 .356 .334 .348 .326 0.341	.098 .092 .094 .088 .090 .088 0.092	.272 .258 .264 .278 .264 .268 0.268	.136 .138 .138 .142 .142 .138 0.139	.098 .098 .094 .098 .092 .090 0.095	.024 .026 .022 .018 .022 .026 0.024
112	.556 .622 .648 .586 .616 .544 0.595	.116 .112 .046 .104 .108 .108 0.110	.484 .444 .462 .498 .458 .476 0.470	.156 .158 .160 .166 .162 .158 0.160	.110 .108 .106 .104 .104 .100 0.105	.032 .038 .034 .028 .034 .038 0.034
140	1.016 1.030 1.110 .928 1.040 .932 1.009	.128 .112 .124 .118 .118 .118 0.120	.580 .542 .594 .614 .558 .620 0.585	.168 .174 .166 .178 .176 .170 0.172	.120 .116 .150 .114 .112 .110 0.114	.036 .040 .036 .028 .036 .038 0.037
168	1.092 1.046 1.142 .960 1.056 .968 1.044	.138 .130 .132 .126 .126 .128 0.130	.592 .554 .610 .628 .572 .638 0.598	.180 .186 .184 .190 .118 .184 0.185	.132 .126 .124 .126 .124 .122 0.126	.040 .042 .038 .030 .038 .042 0.040
228	1.096 1.048 1.146 .962 1.058 .968 1.046	.164 .150 .156 .146 .148 .150 0.152	.592 .552 .610 .626 .568 .634 0.597	.192 .196 .194 .202 .196 .194 0.196	.152 .146 .144 .146 .144 .142 0.146	.040 .044 .040 .032 .040 .044 0.040
350	1.029 1.046 1.142 .962 1.056 .964 1.044	.202 .174 .182 .168 .166 .172 0.177	.590 .550 .608 .624 .566 .632 0.595	.200 .200 .202 .208 .202 .202 0.202	.180 .180 .174 .176 .172 .176 0.176	.046 .048 .040 .034 .044 .046 0.045
404	1.104 1.054 1.148 .970 1.066 .972 1.052	.222 .190 .200 .186 .182 .190 0.195	.594 .560 .616 .612 .574 .640 0.599	.212 .214 .214 .222 .214 .214 0.215	.202 .208 .200 .202 .196 .198 0.201	.056 .060 .052 .046 .056 .058 0.055

TABLE C Sulphate Resistance
Test Results, Cements C and D
CSA CAN3-A5-M77 Test

Aged d	Cement C			Cement D	
	Cement to Slag Ratio By Mass				
	1:0	3:1	1:1	1:0	1:1
	Expansion, %				
14	.016 .020 .018 .020 .022 ~~.034~~ 0.019	.024 .022 .018 .018 .024 .022 0.021	.030 .028 .028 .026 .028 ~~.018~~ 0.028	.030 .028 .032 .032 .030 .028 0.030	.038 .034 .036 .038 .036 .042 0.037
28	.042 .046 .042 .046 .042 .048 0.044	.048 .048 ~~.036~~ .042 .050 .052 0.048	.046 .048 .048 .046 .048 ~~.034~~ 0.047	.038 .038 .040 .038 .038 .036 0.038	.046 .042 .044 .046 .042 .050 0.045
42	~~.048~~ .054 .048 .054 .050 .046 0.050	.052 .050 ~~.038~~ .046 .054 .056 0.052	.054 .054 .054 .052 .056 .044 0.052	.044 .042 .044 .042 .044 .042 0.043	.052 .050 .050 .056 .048 .058 0.052
56	.058 .068 .060 .066 .062 ~~.048~~ 0.063	.060 .058 ~~.044~~ .056 .064 .064 0.060	.060 .060 .060 .058 .060 .052 0.058	.048 .044 .050 .046 .046 .044 0.056	.054 .050 .050 .056 .048 .058 0.053
84	.080 .088 .078 .086 .082 ~~.052~~ 0.083	.078 .080 .066 .078 .086 .084 0.079	.072 .076 .074 .072 .074 .072 0.073	.056 .052 .056 .050 .056 .048 0.053	.056 .054 .056 .060 .058 .064 0.058
112	.098 .104 .094 .100 .094 ~~.052~~ 0.098	.078 .088 .076 .088 .084 .092 0.084	.076 .080 .078 .076 .078 .068 0.079	.072 .066 .072 .066 .070 .066 0.069	.066 .068 .068 .074 .068 .080 0.071
140	.116 .122 .110 .116 .112 ~~.052~~ 0.115	.096 .100 .090 .100 .106 .102 0.099	.084 .088 .084 .082 .086 0.100 0.087	.076 .070 .088 .070 .094 .088 0.081	.068 .068 .068 .076 .068 .078 0.071
168	.140 .146 .132 .140 .136 ~~.060~~ 0.139	.104 .112 .098 .106 .114 .110 0.107	.088 .090 .088 .088 .092 .118 0.094	.086 .078 .082 .080 .080 .076 0.080	.074 .074 .072 .078 .074 .084 0.076
228				.102 .090 .096 .092 .094 .092 0.094	.082 .082 .080 .088 .082 .090 0.084
350				.116 .104 .112 .106 .110 .106 0.109	.084 .088 .082 .090 .086 .096 0.088
404				.130 .118 .124 .120 .122 .122 0.123	.114 .098 .112 .102 .096 .108 0.105

TABLE D Sulphate Resistance Test Results, Cements A', D and D'
Prisms Immersed in Sulphate Solution

Age, d	Cement A'						Cement D						Cement D'	
	Cement to Slag Ratio by Mass													
	1:0		3:1		1:1		1:0		3:1		1:1		1:0	
	H_2O	SO_3	H_2O	SO_3	H_2O	SO_3	H_2O	SO_3	H_2O	SO_3	H_2O	SO_3	H_2O	SO_3
	Expansion, %													
7	.004	.012	.004	.004	.012	.012	.014	.014	~~.016~~	.014	.016	~~.010~~	.016	.016
	.006	.012	.002	.002	~~.016~~	.014	~~.000~~	.010	.008	.010	.016	.014	.012	.014
	.006	.012	.000	.008	.012	.014	.016	.012	.008	.012	.014	.014	.018	.014
	0.005	0.012	0.002	0.005	0.012	0.013	0.015	0.012	0.008	0.012	0.015	0.014	0.015	0.015
14	.016	.022	.012	.012	~~.006~~	.010	.018	.019	~~.018~~	.014	.016	.012	.018	.018
	.016	.022	.010	.010	.012	.010	~~.004~~	.014	.010	.014	.018	.014	.018	.016
	.016	.020	.010	.014	.010	.010	.016	.016	.010	.012	.016	.014	.020	.018
	0.016	0.021	0.011	0.012	0.011	0.010	0.017	0.016	0.010	0.013	0.017	0.013	0.019	0.017
28	.014	.024	.018	.014	.004	.010	.012	.014	~~.014~~	.014	.014	.012	~~.004~~	.018
	.014	.026	.016	.012	~~.010~~	.012	~~.000~~	.016	.006	~~.008~~	.014	.014	.012	.016
	.014	.024	~~.010~~	.014	.006	.010	.010	~~.004~~	.006	.014	.012	.014	.016	.016
	0.014	0.025	0.017	0.013	0.005	0.011	0.011	0.015	0.006	0.014	0.013	0.013	0.014	0.017
56	.006	.028	.002	.010	.008	.002	.016	.024	~~.020~~	.022	.018	.020	.018	.026
	.006	.030	.0 02	~~.004~~	~~.014~~	.004	~~.000~~	.026	.012	.016	.016	.020	.016	.022
	.006	.024	.002	.010	.010	.002	.014	.026	.008	.020	.018	.022	.020	.024
	0.006	0.027	0.002	0.010	0.009	0.003	0.015	0.025	0.010	0.019	0.017	0.021	0.018	0.024
84	.012	.052	.008	.016	.006	.012	.016	.028	~~.016~~	.022	.016	.020	.018	.026
	.014	.056	.008	.014	~~.012~~	.016	~~.000~~	.026	.006	.018	.014	.020	.014	.027
	.012	~~.038~~	.006	.018	.009	.014	.014	.028	.006	.024	.014	.022	.020	.026
	0.013	0.054	0.007	0.016	0.008	0.014	0.015	0.027	0.006	0.021	0.015	0.021	0.017	0.025
112	.006	.076	.004	.016	.002	.008	.016	.040	~~.018~~	.028	.018	.024	.018	.032
	.006	.086	.004	.014	~~.006~~	.012	~~.000~~	.036	.006	.022	.016	.024	.012	.028
	.008	~~.050~~	.004	.018	.002	.010	.012	.036	.006	.026	.016	.026	.018	.030
	0.007	.081	0.004	0.016	0.002	0.010	0.014	0.037	0.006	0.025	0.017	0.025	0.016	0.030
168	.012	.142	.006	.022	.006	.014	.018	.050	~~.022~~	.034	.018	~~.044~~	.020	.040
	.012	.154	.006	.022	.010	.018	~~.000~~	.050	.012	.030	.016	.030	.016	.036
	.012	~~.090~~	.006	.024	.008	.016	.016	.046	.012	.034	.020	.032	.022	.038
	0.012	0.148	0.006	0.023	0.008	0.016	0.017	0.049	0.012	0.033	0.018	0.031	0.019	0.038
224	.018	.222	.014	.030	.016	.026	.020	.060	~~.022~~	.036	.018	.028	.022	.044
	.016	.240	.014	.030	.022	.028	~~.000~~	.060	.010	.030	.014	.030	.016	.040
	.018	~~.150~~	.014	.032	.018	.026	.018	.054	.012	.034	.018	.030	.022	.042
	0.017	0.231	0.014	0.031	0.019	0.027	0.019	0.058	0.011	0.033	0.017	0.029	0.020	0.042
252	.024	.268	.013	.040	.018	.026	.026	.062	~~.028~~	.036	.024	.026	.028	.044
	.022	.288	.018	.038	.022	.030	~~.006~~	.066	.018	.030	.022	.028	.022	.040
	.026	~~.186~~	.018	.040	.018	.026	.024	.058	.018	.036	.024	.032	.032	.042
	0.024	0.278	0.016	0.039	0.019	.027	0.025	0.062	0.018	0.034	0.023	.029	0.027	0.042

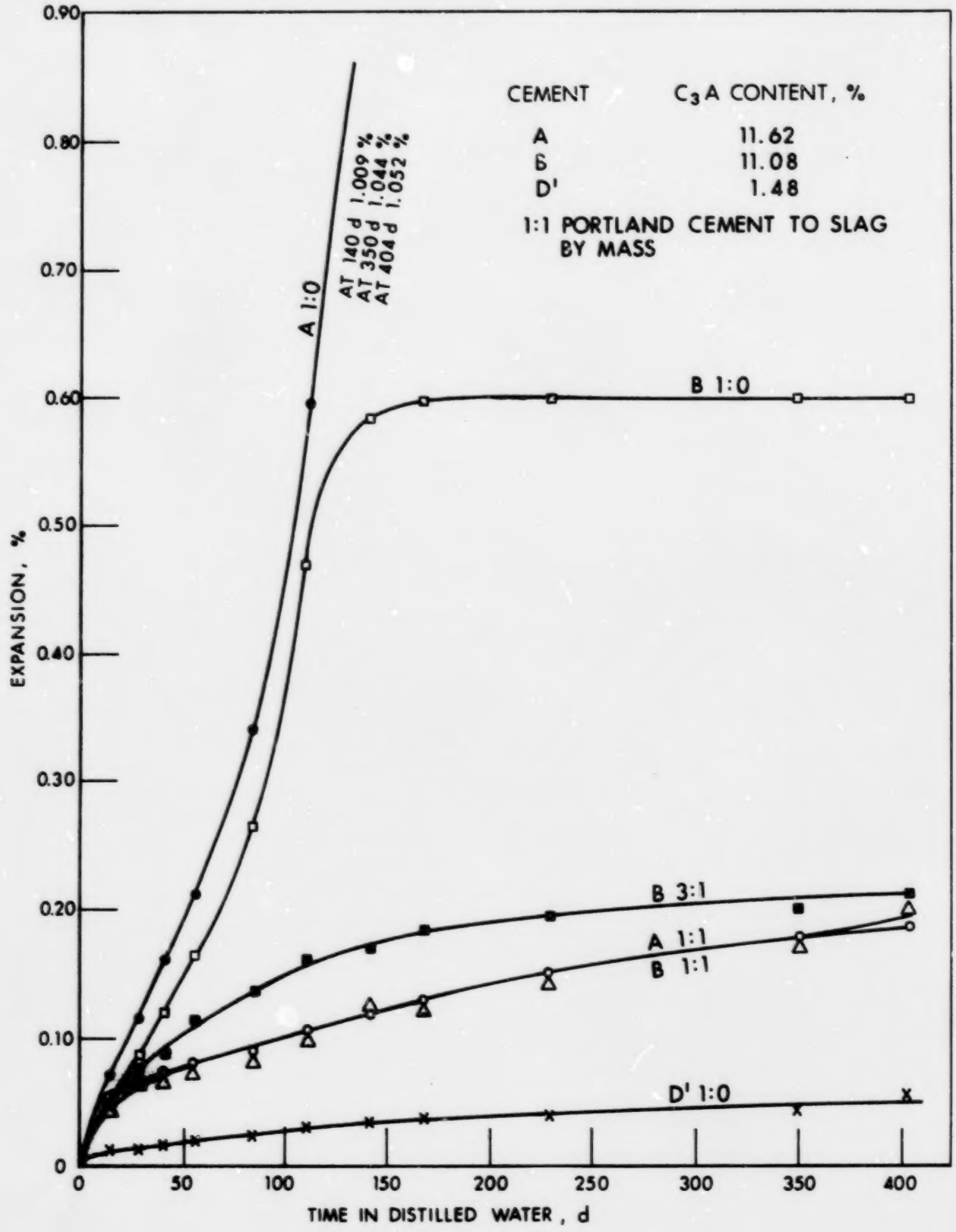

FIG. 1 - SULPHATE RESISTANCE OF PRISMS WITH CEMENTS A, B & D', STANDARD TEST

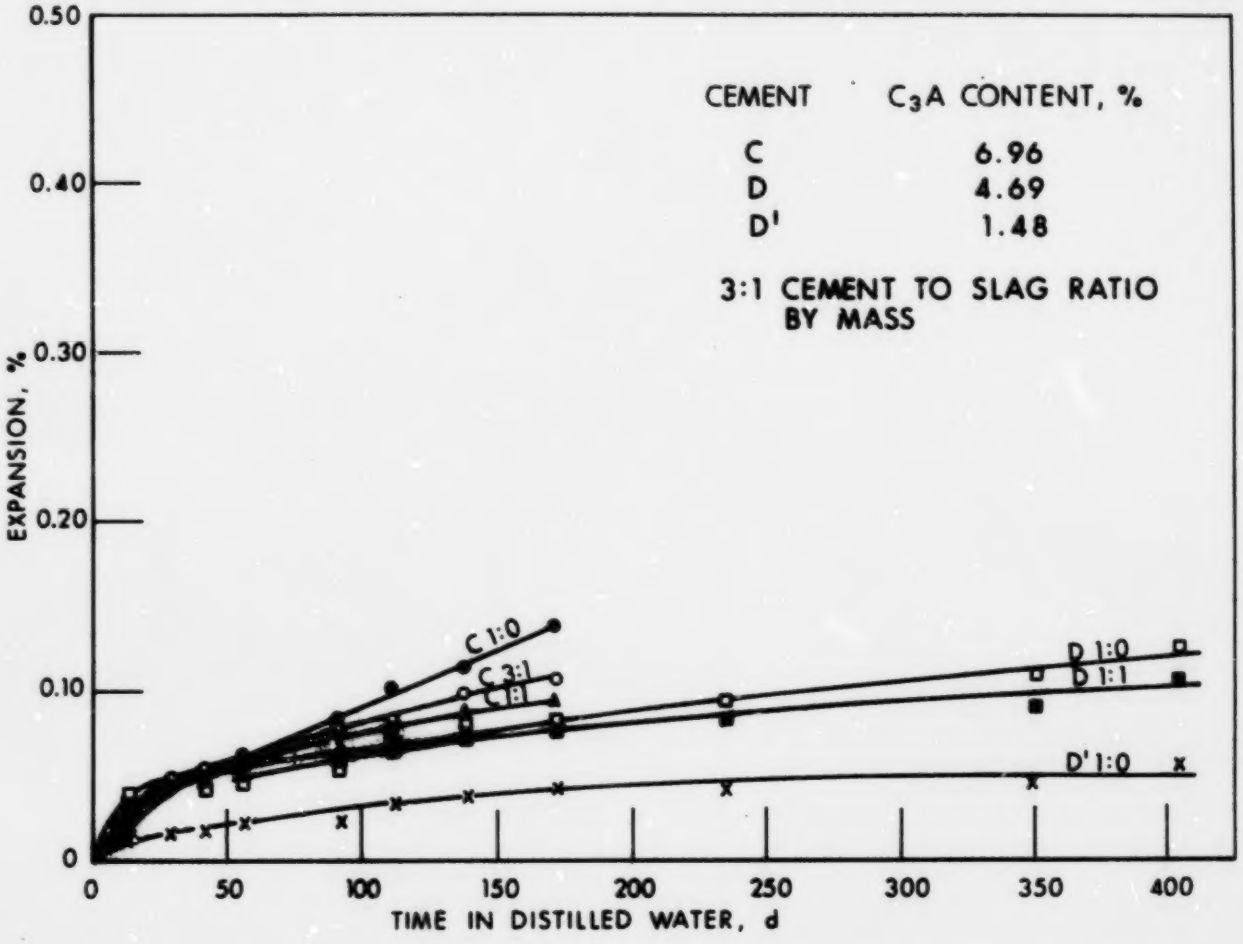

FIG. 2 - SULPHATE RESISTANCE OF PRISMS WITH CEMENTS C, D & D', STANDARD TEST

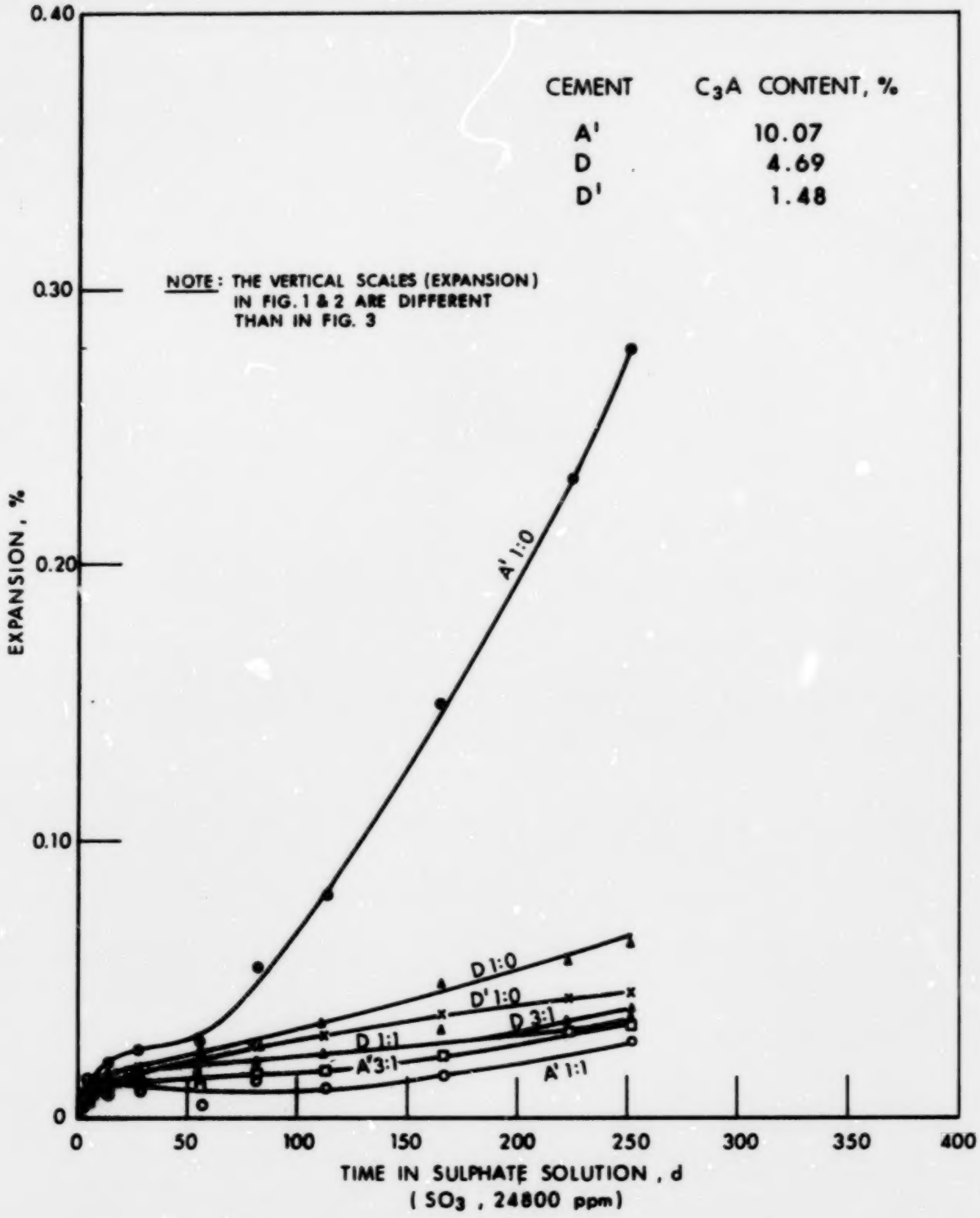

FIG. 3 - SULPHATE RESISTANCE OF PRISMS WITH CEMENTS A', D & D'